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A STUDY OF THE DETERIORATION OF ADHESIVES IN METAL BONDS AT HIGH TEMPERATURES

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ABSTRACT

The thermal resistance of clad aluminum bonded with FPL-878, a phenol-epoxy resin adhesive, was decreased markedly by progressively longer precure periods and higher precure temperatures. Bonds made with FPL-878 under the optimum conditions of metal preparation and precure showed relatively small decreases in strength after 200 hours of aging at 550° F. Thermal resistance of FPL-878 in bonds of stainless steel was improved by coating chemically treated stainless steel with zinc naphthenate and heating to 1,200° F.

Aging of aluminum bonds at 300° and 400° F. under stress increased the strength of bonds later tested at -70° and 80° F. by as much as 30 percent. Cycling of bonded aluminum and stainless steel between temperatures of 450° and -55° F. produced no evidence of failure caused by thermal shock or differences in expansion between adhesive and adherend.

A study of the chemical changes in FPL-891, a phenol-epoxy resin adhesive, when aged at 550° F. in air and nitrogen was made by infrared spectrophotometry. A qualitative interpretation of the results showed a significant increase in absorption in the carbonyl region of the spectra during aging. These changes occurred more rapidly in air than in nitrogen.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

AIDRO LINGARD, Colonel, USAF
Chief, Aeronautical Research Laboratory
Directorate of Research

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INTRODUCTION

The purpose of this study was to perform related research to reveal, if possible, the mechanism of observed deterioration of organic-base adhesives employed in metal-to-metal bonds in service at elevated temperatures.

The work involved a study of the performance characteristics of laboratory-formulated phenol-formaldehyde-epoxy resin adhesives that had been shown by previous work[1] to be one of the more heat-resistant type of adhesives for bonding metal. An attempt was made to find the possible causes of chemical and physical changes that might be associated with the deterioration of an adhesive in metal bonds in service at elevated temperatures. The thermal resistance of adhesive bonds in aluminum and stainless steel as affected by preparation of the metal surface, curing conditions, aging temperature, aging time, atmosphere during aging, and stress during aging was investigated.

STUDIES BY INFRARED SPECTROPHOTOMETRY

In this phase of the work, unsupported films of the adhesive were analyzed by infrared absorption to observe the changes in the chemical structure of the adhesive with progressive curing and aging at elevated temperatures. It was recognized that the application of the infrared absorption technique to complex materials such as highly polymerized phenol-epoxy resin adhesives would serve only as a qualitative measure of gross chemical changes occurring in the adhesive.

The absorption spectra of the various adhesive films were determined on a double-beam infrared spectrophotometer in the 2- to 16-micron region.

Preparation of Films

After considerable experimentation, the most satisfactory method for preparing unsupported adhesive films, suitable for infrared analysis, was solvent casting of the adhesive on a polished glass plate. Dry films about 0.001 inch thick were obtained consistently by casting a wet film of the adhesive on the glass surface by means of an accurately machined doctor blade designed to give a wet film 0.002 inch thick.

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[1] Black, J. M., and Blomquist, R. F. Development of Metal-Bonding Adhesives with Improved Heat Resistant Properties, Final Report. NACA Order No. W-5756, April 11, 1953. Report submitted to NACA in September 1954.

NOTE * This Technical Report was released by the author for publication in June 1955.

The solids content of the adhesive was reduced to 60 percent by thinning with ethyl acetate before casting. The cast films were then precured and cured as desired on the glass plate by heating in ovens or on the platens of a press. To remove the film from the glass plate, the cured film was immersed for 1 day in distilled water and then removed from the glass with a sharp razor blade. The films were then dried in vacuum at room temperature for 16 hours prior to analysis. The dried films were mounted over a 1- by 2-inch opening in an aluminum film holder to hold the film in place during subsequent heat aging and spectrophotometric analysis.

Results of Infrared Absorption Studies

The initial work was conducted on a simple adhesive formulation, FPL-891, (Appendix), composed of 12.5 parts by weight of phenol resin (Durez 16227) and 2 parts by weight of epoxy resin (Epon 1001) in 2 parts by weight of ethyl acetate solvent. Later studies included more complex formulations employing curing agents and thermal stabilizers.

The infrared absorption spectra of typical films of FPL-891 adhesive after initial precure, cure, postcure, and aging at 550° F. in nitrogen and in air are shown in figures 1 and 2. All results reported were from analyses on portions of a single film, cast and cured at one time and then separated into portions for further treatment and exposure as indicated.

The most significant change in the absorption spectra with curing, postcuring, and aging at 550° F. was the increased absorption occurring between 6.0 and 6.3 microns and the broadening and shift of this band to the left with more cure and heat aging of the film. The band at 6.1 microns after curing for 60 minutes at 300° F. in air (fig. 1-B) increased markedly in absorption from about 48 percent transmission when precured (figure 1-A) to 25 percent transmission and has shifted to include absorption at 5.8 microns. Aging of the postcured film for 30 minutes at 550° F. (fig. 2-A) shifted the band further, and aging the film for 16 hours at 550° F. in air (fig. 2-B) shifted the band to include absorption at 5.4 microns. The absorption in this range of infrared wave lengths (5.4 to 6.3 microns) is attributed to carbonyl groups such as are found in organic acids, anhydrides, lactones, quinones, esters, aldehydes, and ketones, or to the formation of unsaturated acetylene and ethylene groups. Some of these functional groups are possible products of oxidation and thermal degradation.
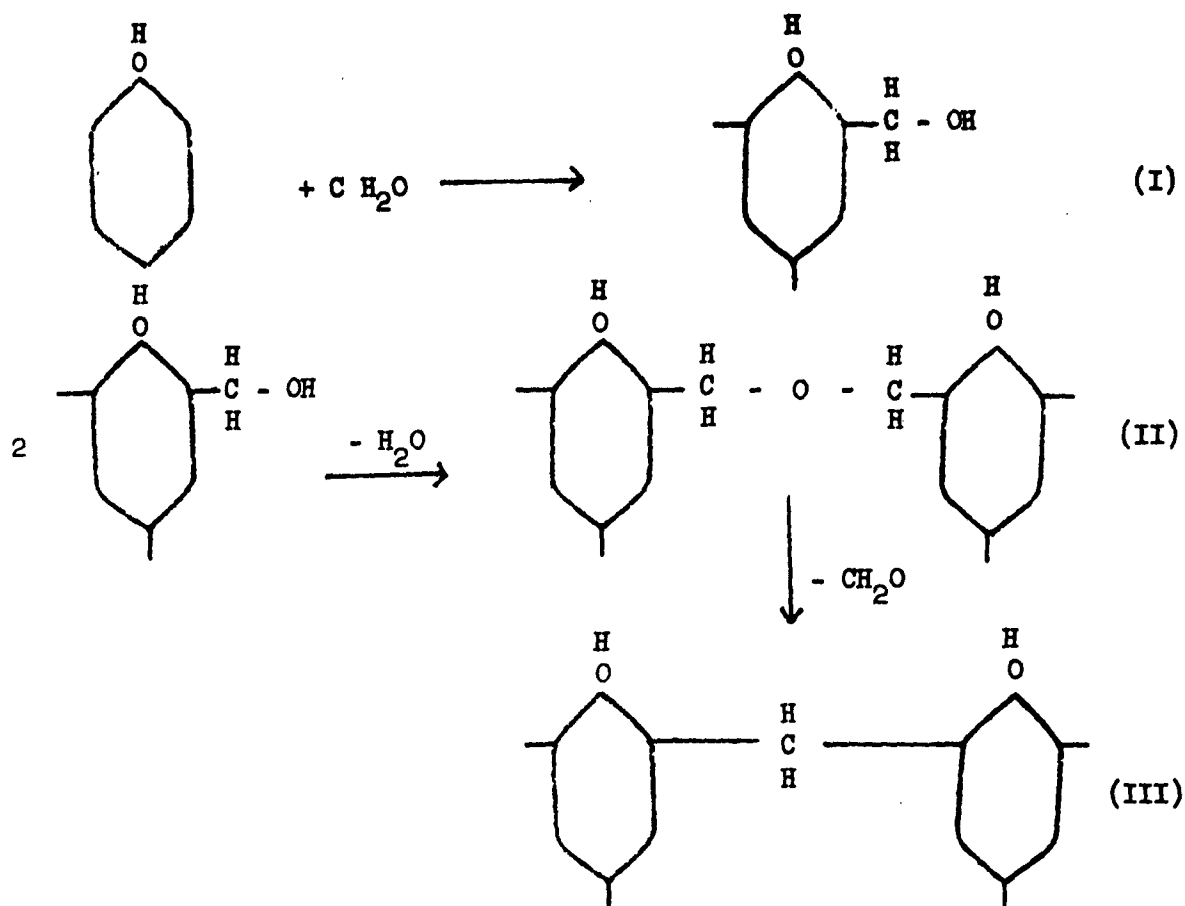
Aging of the film in nitrogen at 550° for 16 hours (fig. 2-C) instead of air (fig. 2-B) without a previous postcure in air resulted in less broadening or shifting of the absorption band in this region, indicating that oxygen from the air may have contributed significantly to the formation of various carbonyl and unsaturated groups. It was also

observed that the absorption spectrum obtained when films were aged for 16 hours in nitrogen at 550° F. (fig. 2-C) was almost identical to the absorption curves obtained when the films were postcured for 16 hours at 270° F. and aged for only 30 minutes at 550° F. in air (fig. 2-A).

The absorption of infrared at 3.0 microns, attributed to hydroxyl groups, showed a gradual decrease as the cure of the adhesive advanced through the cure, postcure, and aging stages. At about 3.0 microns the percent transmission of infrared radiation was increased from 8 to 14 percent by curing 60 minutes at 300° F., a further increase to 17 percent by post-curing for 16 hours at 270° F., an increase to 20 percent by aging 30 minutes at 550° F., and to 25 percent transmission by aging 16 hours at 550° F. in air. This increase in the transmission of infrared indicates a decrease in the number of hydroxyl groups, which could very well be related to the conversion of methylol groups in the partially cured resin to ether groups and finally to methylene crosslinkages in the cured poly-mer. This reaction would be expected to show a rather rapid loss in hydroxyl groups during the early stages of cure and a considerably slower rate of change with temperature and time after a high degree of cure is obtained. Such a correlation appears in these data in that heating for 1 hour at 300° F. increased the transmission in the hydroxyl region from 8 to 14 percent, while heating for 16 hours at 550° F. beyond the 30 minutes at this temperature increased the transmission of infrared only from 20 to 25 percent.

The absorption spectra at 3.5 microns, which is normally attributed to stretching of the carbon-hydrogen bond, showed decreases in adsorption somewhat similar to those of the hydroxyl groups as cure and heating pro-gressed. In figure 1 the percent transmission in this region after pre-cure was about 17 percent (1-A), after cure 19 percent (1-B), after post-cure 21 percent (1-C), after 30 minutes at 550° F. 20 percent (2-A), and after 16 hours at 550° F. in air about 35 percent (2-B). These values re-flect a decrease in the number of carbon-hydrogen bonds as cure pro-gresses, which might be expected to change very slowly in the initial stages of cure and postcure and then show a very rapid change after aging at 550° F. for 16 hours. It would seem that the observed changes in the relative quantity of carbon-hydrogen groups in these tests could be correlated with the theoretical changes in the structure of the phenol resin during cure and thermal degradation as described by Carswell.[2] He has recognized that the curing reactions of phenol and formaldehyde are rapid and complex at normal curing temperatures and the extent to which the various reactions take place depends upon the structure of the inter-mediate phenolic compounds formed, temperature and time of the reactions, and the catalyst system. The following curing reactions therefore, prob-ably represent the more simple steps in the cure of a phenolic resol resin.

[2] Carswell, T. S. Phenoplasts, Their Structure, Properties, and Chemical Technology, Interscience Publishers, Inc., N. Y., 1947.

H
O

$+ C H_2O \longrightarrow$

H
O
H
C - OH
H

(I)

H
O
H
C - OH
H

2

$- H_2O \longrightarrow$

H
O
H
C - O - C
H   H
H
O

(II)

$\downarrow - CH_2O$

H
O
H
C
H

H
O

(III)

In the initial stages of cure the methylol groups of the phenol deriva-
tive (I) condense to form dibenzyl ether groups (II) without a change
in the number of C-H groups. In the next step of cure the ether groups
are believed to split off a molecule of formaldehyde to form a single
methylene bridge between phenol molecules (III). Hanus[2] reported that
even under the most favorable conditions not more than 60 percent of
this theoretical amount of formaldehyde could be liberated from the
system. This was attributed to the tendency of formaldehyde that was
liberated momentarily to combine further with methylene groups of the
diphenylmethane derivative (III) and other possible side reactions.
Thus one would expect little change in the number of C-H groups of a
resin on exposure to typical curing and postcuring conditions. The
exposure of the resin to extreme temperatures, such as 550° F., how-
ever, could result in thermal decomposition of the material; this may
result in rupture of the methylene bridges with the formation and lib-
eration of carbon dioxide and hydrogen. Such a mechanism has been

proposed by Allen, Meharg, and Schmidt[2] who studied the decomposition products of phenol resin at 300° C.

Another change in the infrared absorption spectra of the phenol-epoxy resin adhesive with increased heating was the disappearance of the band at 12.1 microns, which is attributed to the para-substitution present in the original molecule of bisphenol of the epoxy resin[2] This band had disappeared after aging for 16 hours at 550° F. in air, showing that some thermal decomposition was also taking place within the epoxy resin.

In other experiments, separate portions of one cured film of FPL-891 adhesive were aged at 550° F. between two pieces of aluminum and between two pieces of stainless steel. The aluminum surfaces had been prepared by the sulfuric acid-sodium dichromate process and the stainless steel surfaces were prepared by sulfuric acid-oxalic acid process described in the Appendix. The pieces of metal were clamped tightly against the film to determine, if possible, any effects of the metal surfaces on changes occurring in the adhesive when heated. Changes in spectra that normally were found to occur when films were aged in air were greatly reduced when films were aged in contact with the metal surfaces. There were no noticeable differences in the films exposed next to aluminum and next to steel. The reduced amount of deterioration of these films was attributed to the exclusion of the air from the film.

Infrared studies of films of FPL-891 adhesive that also incorporated 1 percent by weight of either quinolinol, copper-quinolinol, or n-propyl gallate as thermal stabilizers, showed no apparent chemical changes in films caused by the use of these materials. These materials had in previous work[1] shown some promise as effective agents in reducing thermal deterioration in adhesive bonds. In this study the films were aged in air at 550° F. for periods up to 16 hours.

The study of the thermal decomposition of a phenol-epoxy adhesive film by infrared absorption has shown that if the adhesive is exposed to air at elevated temperatures, the adhesive undergoes marked changes in chemical structure. These changes are apparently accelerated by the oxygen in air. Little correlation could be found between these observed changes in adhesive films exposed to hot air and actual changes in the performance of adhesive bonds in aluminum and stainless steel that were heated for similar periods of time. The difference in performance between films and adhesive bonds of metal was presumably due to a high degree of exclusion of the air from the adhesive films in the metal joints.

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[3] Harms, D. L., Analyt. Chem. 25, 1140 (1953).

DETERIORATION OF METAL BONDS IN NITROGEN AND AIR

This phase of the study was intended to study possible correlations of
the chemical changes in films after exposure to high temperatures, as
observed by infrared spectrophotometry, with the performance of adhesive
bonds of aluminum and of stainless steel under similar conditions of
heat aging. It was also hoped that the study of strength properties of
metal-to-metal bonds would give an insight into the possible effects of
such variables as the chemical nature of the metal surface on the thermal
stability of the adhesive bond.

Preparation of Bonds

Unless otherwise noted throughout this entire report the joint test
specimens were 0.5 inch lap shear specimens of either 0.064 inch 24ST-3
clad aluminum alloy or of 0.020 inch thick T302, 1/2 hard stainless
steel. Aluminum specimens were bonded in panel form and then cut care-
fully into individual specimens, each 1 inch wide. Because of the dif-
ficulty of sawing individual specimens of stainless steel from panels
after bonding without damaging the bonds, a different procedure was used
here. In the earlier work, steel sheets for multiple panel bonds were
slit down from one edge before bonding so that all that was required to
separate bonded specimens for test was to cut away a short strip at the
ends of the specimen. In later studies, individual stainless steel
coupons were bonded directly with a suitable jig to maintain alinement.

For the investigation of the deterioration of bonds in nitrogen and in
air, the aluminum and stainless steel lap joints were bonded with the
same batch of FPL-891 adhesive as was used in the study of films by in-
frared absorption. The surfaces of the aluminum and steel were prepared
for bonding by first wiping the metal surfaces with a clean cloth satur-
ated with ethyl acetate. The aluminum was then treated chemically by
Method A (Appendix) and the steel by Method B (Appendix). The adhesive
was brush spread on the treated metal surfaces on the same day as the
metal was prepared and the coated surfaces precured for 15 minutes at
270° F. The metal panels were then assembled and pressed at 50 pounds
per square inch for 1 hour at 300° F. and postcured for 16 hours in air
at 270° F. without external pressure. The panels (20) were cut into
specimens 1 inch wide; the specimens were then selected by the random-
ized block method for each of the test conditions. The shear strength
of the lap-joint specimens was determined by loading at a rate of 1,200
to 1,400 pounds per square inch per minute (the method described in
Military Specification MIL-A-8331(USAF): Adhesive, Aircraft Structural,
Metal-to-Metal, June 26, 1953). The bonded lap joints were tested in
shear at room temperature after the postcure of 16 hours at 270° F. to
obtain the initial shear strength of the bonds for control purposes;
other representative groups of 10 specimens each were set aside for

exposure in air and in nitrogen at 550° F. before cooling and testing at room temperature. The lap joints to be aged in nitrogen were placed in a tight metal cylinder; a slight pressure of nitrogen was applied to exhaust the chamber of air and volatile byproducts and to provide an atmosphere of an inert gas. The nitrogen was passed through sulfuric acid drying trains before being introduced into the chamber.

Results of Aging in Air and Nitrogen

The results of tests at room temperature of lap joints of aluminum and stainless steel after aging for various periods at 550° F. in air and nitrogen are shown in table 1.

The results of these tests showed conclusively that the type of metal, method of metal surface preparation, and the atmosphere of exposure had marked effects on both the initial strengths of the bonds and also on the strengths of bonds after aging at the elevated temperature.

The performance of bonds of aluminum showed that the initial strength of bonds before aging was greatly affected by the treatment of the surface prior to bonding. An oxidizing chromate solution (Method A), which could presumably produce an aluminum oxide layer on the bonding surface, gave much higher initial strengths before heat aging than did a reducing treatment (Method B), which might presumably remove the naturally occurring aluminum oxides from the bonding surface. The aluminum joints prepared by Method A, although higher in strength after aging for 96 hours in air than the bonds prepared by Method B, were reduced in strength approximately the same amount from the initial strength values. This would indicate that the strength of bonds after aging at elevated temperatures is closely related to the initial bond strength and to the bonding characteristics of the metal surface.

The data on aluminum specimens showed that the principal reduction in joint strength due to aging occurred within the first 96 hours of exposure and further aging up to 200 hours had very little effect, if any, on joint strength. The fact that there were no important progressive losses of strength of the aluminum specimens in heat aging beyond 96 hours in either air or nitrogen, and that there was very little severe charring or discoloration in the bonds after these tests suggests that the losses of joint strength during the first 96 hours of aging may more likely have been due to further cure and embrittlement of the adhesive rather than to actual thermal deterioration of the phenol-epoxy resin adhesive. This lower level of strength noted here after heat aging, has also been noted previously with this type of adhesive when bonds were cured initially at higher temperatures, such as 350° F., a condition assumed to cause embrittlement and internal strains due to a high degree of cure without actual polymer degradation. The color of the bonded areas after test also indicated that 200 hours aging at 550° F. in a

bond was considerably less severe in discoloration and possible thermal degradation than aging, in the film form, for 16 hours at 550° F. in air or nitrogen as was done in the study of unsupported adhesive films by infrared absorption.

The bonded areas of the aluminum specimens after heat exposure and test were examined microscopically. Within a typical bond area a network of minute tunnel-like voids were visible that extended in from a bubble in the squeezeout at the edge of the joint toward the center of the bonded area (fig. 3). The minute tunnels were apparently formed by the loss of volatile materials during the bonding process, as they were visible in both aged and unaged specimens. Discoloration of the adhesive film by heat aging was evident along the walls of the tunnels, but it extended back into the adhesive mass only a very short distance; this depth of penetration was not noticeably increased as the exposure period was increased from 96 to 200 hours. In other work on a similar type of adhesive, discoloration in the tunnel walls has been observed after only 4 hours aging at 550° F. but without appreciable increase in depth by extending the exposure to 200 hours. The discoloration and thermal decomposition of the adhesive in these areas was believed to have been caused by residual volatiles consisting probably of solvent, ammonia, water, formaldehyde, and phenol, that were volatilized during cure but remained in the tunnels.

The evidence thus indicated that there should be little thermal deterioration of FPL-891 phenol-epoxy resin adhesive in bonds of aluminum at 550° F. after 200 hours if the metal surface has been prepared properly and certain undesirable volatiles are removed.

The performance of FPL-891 adhesive, aged at 550° F. in bonds of stainless steel, differed in many respects from that in bonds of aluminum. The data in table 1 showed that in addition to the type of surface preparation, the atmosphere of exposure was highly important in affecting the thermal resistance of the adhesive bonds. For stainless steel the sulfuric acid-oxalic acid method of surface treatment gave better initial bond strength and better thermal resistance properties than the sulfuric acid-sodium dichromate process. The reverse was true for bonding of aluminum. This would indicate that for aluminum FPL-891 bonds best to an oxidized surface, and for stainless steel it bonds best to a reduced surface.

The presence of air during the aging cycle obviously contributed to the breakdown of the adhesive in stainless steel bonds. Examination of the stainless bonds after heat aging and testing showed that discoloration of the adhesive started at the edges of the lap joint and progressed inward as longer aging periods were employed. The rate of discoloration was much lower when bonds were aged at 550° F. in nitrogen, and higher joint strengths were retained, particularly when Method B was used in preparing the metal for bonding.

The generally inferior performance of stainless steel bonds on heat aging compared to that of aluminum bonds might be evidence that the metal itself contributes to degradation of the adhesive. It is possible that oxides of iron, nickel, or chromium are formed in the surface layers of the steel during heat aging of the bonds and may act as catalysts for the subsequent deterioration of the adhesive in contact with these metal surfaces. The progressive discoloration of the adhesive inward from the edges of the steel bond might be interpreted as further evidence of the adverse effect of the stainless steel surfaces inasmuch as a similar progressive type of breakdown of the adhesive was not observed on aluminum. These hypotheses served as a basis for much of the later work in this study.

FURTHER STUDIES OF THE DETERIORATION OF ALUMINUM BONDS

The preliminary study of the thermal deterioration of FPL-891 adhesive by infrared absorption of unsupported films and in aluminum and stainless steel bonds revealed that the resistance of the adhesive to thermal degradation in an aluminum bond prepared under optimum conditions was quite high and apparently was not closely related to the rapid oxidation observed in an unsupported film in air at elevated temperatures. However, in previous work on the development of heat-resistant adhesives[1] it was shown that not all aluminum bonds made with phenol-epoxy resin adhesives were resistant to thermal degradation. The preparation of the metal surface for bonding and the bonding conditions used were important variables and had to be controlled within certain limitations. A more complete explanation of the causes and effects of these variables was needed to understand fully their influence on the resistance of an adhesive bond to thermal degradation.

This phase of the study was conducted on FPL-878 adhesive, a phenol-epoxy resin formulation, (Appendix) in 0.5 inch lap shear joints of 0.064-inch-thick 24ST-3 clad aluminum alloy. This adhesive was known to have somewhat higher resistance to thermal deterioration than the simpler FPL-891, used in the previous study, when employed under optimum bonding conditions.

Effects of the Condition of the Metal
Surface Prior to Bonding

Various chemical and electrolytic methods were used in preparing the surface of the clad aluminum alloy for bonding. Surfaces with distinctly different physical appearances or surfaces assumed to be chemically different were obtained. The results of tests of bonds to these surfaces gave further insight into the problems of both the adhesion characteristics of the metal surface and the effect of the metal surface on the resistance of the adhesive to thermal degradation. The

results of lap shear tests at room temperature of heat-aged and unaged specimens bonded with FPL-878 adhesive at 320° F. for 60 minutes after a precure of 30 minutes at 200° F. are shown in table 2.

The aluminum bonds prepared by the first four methods shown in table 2 -- A-1, A-2, A-3, and A-4 -- all appeared to have similar strength properties initially and also after aging at 550° F. for 48 hours. These methods of preparing the aluminum for bonding etched the surface noticeably and therefore could be considered as effective in increasing the surface area. Presumably they were also effective in removing the aluminum oxide layer from the original surface and in leaving a rather pure metallic aluminum surface for bonding, at least momentarily. The sub-sequent drying of the treated surfaces at room temperature and short storage (less than 24 hours) before bonding would probably allow a new oxide layer to form, but this would be expected to be a comparatively shallow oxide layer compared to the oxide layers intentionally formed by other oxidizing chemical and electrolytic methods. In some cases the metal surfaces were heated at 550° F. after the chemical etching to dry the treated surfaces thoroughly and to help remove absorbed gases, acids, or alkalies from the surface that might adversely effect the bonding or aging characteristics of the adhesive. The possible effects of such heat treatment on the physical properties of the metal are not known. The data showed that heating the metal for 1 hour at 550° F. before bonding was of no particular advantage in the methods A-1, A-2, A-3, and A-4, indicating that any adsorbed chemicals from the treating solution had probably been adequately removed by the standard rinse in tap water and distilled water.

The aluminum prepared by immersion in a solution of sulfuric acid and sodium dichromate (Method A-5 or Method A in Appendix) developed bonds of somewhat higher initial strength and significantly greater resist-ance to thermal degradation than those obtained by methods A-1, A-2, A-3, and A-4.

The results of tests employing method A-5 compared with method A-3 show the value of using sodium dichromate in sulfuric acid solutions to improve the bonding surfaces. The improved bonding surfaces pre-sumably come about as a result of the strong oxidizing power of sodium dichromate in the presence of sulfuric acid to form an aluminum oxide layer, under controlled conditions, that has improved adhesion and co-hesion characteristics. Because the oxide layers formed by such con-trolled chemical means are known to be highly adsorptive, the adsorp-tion of acid from the chemical treatment as a result of inadequate washing of the surface is likely to be a problem. The effect of ad-sorbed acid is shown by the results of tests on metal prepared by method A-5b where the metal was rinsed in 1 percent sulfuric acid solu-tion and then air dried following the regular immersion in the sulfuric acid-sodium dichromate solution. These bonds were significantly low in initial strength and in resistance to thermal degradation. In method

A-5c, a modification of the sulfuric acid-sodium dichromate method, the metal surfaces were placed in boiling water for 1 hour before bonding. This treatment of the aluminum is considered by aluminum manufacturers to have a sealing action on the porous aluminum oxide by converting it to the monohydrate, which effectively closes the pores and destroys the adsorptive and high adhesion characteristics of the surface. The result of tests on joints prepared by method A-5c tend to confirm this, as shown by the low initial strengths of joints as compared to those prepared by method A-5. The introduction of water into the oxide layer to form the monohydrate also reduced the resistance of the adhesive to thermal deterioration.

An electrolytic chromic acid anodize treatment, which also forms an oxide layer on the aluminum surface, was used in methods A-6, A-6a, and A-6b followed by rinsing in water (A-6), heat treating at 400° for 1 hour (A-6a), and sealing in boiling water (A-6b). Results of tests of specimens prepared by these methods show that the anodizing method was particularly effective in promoting good adhesion, except when water sealing was used. Resistance to thermal degradation was high when the metal was heat treated for 1 hour at 400° F., but very low when water sealed to form the hydrated oxide film.

A reducing type treatment employing sulfuric acid and oxalic acid (method A-7) which would be expected to remove the corrosion-resistant aluminum oxide layer resulted in bonds that had good initial strength but were low in resisting thermal degradation.

The results of the work on surface treatment of aluminum before bonding showed that an aluminum oxide surface is one of the most desirable surfaces for bonding to promote high initial strength and resistance to thermal degradation. Small amounts of residual acid or even absorbed water will seriously reduce the initial adhesion and the thermal resistance of the bond.

Effect of Precuring Conditions

In addition to the preparation of the metal surfaces for bonding, one would also expect the conditions for assembly and bonding in the process of making a metal bond to be highly important variables in the performance of an adhesive at elevated temperatures. Based on earlier work[1] and also on further work in the present study it seemed that the precuring process was probably one of the most critical phases in the bonding procedure as it affected the thermoplastic properties of the adhesive at elevated temperatures and the resistance of the bond to heat aging. A precure is generally employed with solvent-type adhesives to

remove solvents to prevent the formation of bubbles of volatile materials and voids in the bond during the subsequent cure of the resin in the pressing operation. In addition to poor initial bonds due to blistering in hot pressing, the presence of these entrapped solvents and other volatiles in the joint has also been considered as having an adverse effect on the adhesive film during heat aging. Since the solvents usually employed in adhesives are quite volatile, the most effective and practical way to remove them from the adhesive film would appear to be to dry or precure at as high a temperature, and for as long a period as possible without adversely affecting the resin components by overcure and reduced flow properties.

A study of the effects of precure on the resistance of a phenol-epoxy adhesive, FPL-878, showed that the complete removal of solvents by adequate precure is probably not the most important change that occurs during the precuring period. The following test data for aluminum bonds, of the lap-shear type bonded with this adhesive, illustrate how the precure temperature and the length of time of precure influenced both the resistance of the bond to thermal degradation, as shown by the strength of joints after aging 16 hours at 550° F., and the resistance of the bond to thermal softening, as shown by the strength of joints tested immediately at 500° F. The metal was prepared by Method A (Appendix) and bonded for 60 minutes at 320° F. under 50 pounds per square inch pressure.

Precure conditions		Shear strength[1]	
Time:	Temperature:	At 80° F. after 16 hours at 550° F.	Immediately at 500° F.
Min.:	° F.	P.s.i.	P.s.i.
30 :	200	1,286	1,246
60 :	200	1,066	....
20 :	250	1,174	1,020
40 :	250	598	660
60 :	250	576	210
10 :	275	1,082	1,060
15 :	275	984	600
25 :	275	366	264

[1] Each value is the average of 5 test specimens.

The results of these tests showed that as the period of time at a given precure temperature was increased, the resistance of the adhesive to

thermal degradation (as shown by the strength at 80° F. after 16 hours at 550° F.) was decreased. The reduced strength after heat aging was accompanied by very marked evidence of thermal deterioration of the adhesive as indicated by the presence of discolored areas in the bond. The strength of bonds tested immediately at 500° F. without aging was also decreased as the precure time was increased. The latter affect could be interpreted as indicating a reduction or modification in the degree of crosslinkage with a resultant increase in thermoplasticity of the adhesive. The adverse effects of the longer precure periods were not considered as resulting from advanced cure of the resin with subsequent poor flow and inadequate fusing of the faying surfaces during the pressure and curing cycle since all bonds had very similar satisfactory strengths initially at room temperature, and the appearance of the bonds in initial tests indicated adequate flow of the adhesive during bonding. Neither is it likely that more complete removal of solvent from the adhesive by the longer precure periods could have an adverse effect since the solvent presumably has no known role in the crosslinkage and curing reactions of the resins.

Study of the bond areas after test revealed that there was a reduced amount of branching or fewer tunnel-like passages (fig. 3-B) for escape of volatiles in the specimens that were precured for the longer periods, particularly when precured at 250° and 275° F. It was also observed that joints with lower strengths after aging always had dark brown or black spots of deteriorated adhesive in the bond as shown in fig. 3, C and D. These spots occurred in bonds with longer precure, particularly at 275° F. and were located both within the bonded area as well as at the edges of the bond. The spots were round and oval shaped and appeared to have been formed by progressive deterioration starting from a single nucleus, as the center of the spots were frequently darker in color than the surrounding area. The spotted areas of discoloration were never noted when bonds, precured at 200° F., were heat aged.

Since adverse precure conditions resulted in both a loss in resistance to thermal degradation and a loss in the immediate strength of joints at elevated temperature, one logical explanation for this behavior appeared to be that some crosslinking agent or thermal stabilizer was lost by volatilization during the more severe precure conditions.

One adhesive component, considered most likely to be influenced by heat, is formaldehyde, which is an important crosslinking agent for phenol resins. If unreacted formaldehyde were lost excessively during the precure, it could result in a lower degree of crosslinkage and a loss in strength at elevated temperatures. To investigate this possibility, additional formaldehyde was added to FPL-878 adhesive by adding hexamethylenetetramine and allowing it to react with the adhesive by refluxing for various lengths of time before application. In this work it was assumed that the longer refluxing of the adhesive components

would advance the cure of the resins slightly and might also partially
react the formaldehyde and the resins to make the formaldehyde more
stable and less likely to be driven off by subsequent heating during
precure. This hypothesis was not substantiated by the following results
of tests made on conventional lap joints of aluminum with this modified
formulation of FPL-878 containing 5 percent hexa.

Precure conditions		: Amount of hexa[1]	: Reflux time[2]	: Shear strength[3]
Time : Temperature :		:	:	:
Min. :	°F.	: Percent	: Min.	: P.s.i.
30 :	200	: 0	: 15	: 1,388
30 :	200	: 0	: 120	: 1,754
30 :	200	: 5	: 15	: 1,276
30 :	200	: 5	: 120	: 912
15 :	275	: 0	: 15	: 824
15 :	275	: 0	: 120	: 542
15 :	275	: 5	: 15	: 448
15 :	275	: 5	: 120	: 664

[1] Percent by weight of hexamethylenetetramine
   based on resin solids of FPL-878.

[2] Reflux time refers to the time all adhesive
   components of FPL-878 were refluxed to-
   gether at steam bath temperature.

[3] Tested at room temperature after 16 hours
   at 550° F. Each value is the average of
   5 specimens.

The addition of hexa did not significantly improve the thermal resist-
ance of bonds precured at either 200° or 275° F. and in some cases
appeared to have an adverse effect. The length of time of refluxing
had no consistent, marked effect in either increasing or decreasing the
resistance of bonds to aging at elevated temperatures. These data in-
dicate that the loss of formaldehyde during the more severe precure
conditions was probably not the real cause of reduced immediate strength
at elevated temperatures or the lowered resistance to thermal degrada-
tion. In this experiment the precure conditions were again the most
significant bonding variables that influenced the thermal resistance of
FPL-878 adhesive.

Another possible explanation for the adverse effects of the higher pre-
cure temperature and longer precure period may be the formation of un-
desirable organic peroxides or other intermediates as by oxidation of

residual solvents and other adhesive components in the adhesive film
during the open exposure to heat and air drying during the precure
period. These reaction products could be expected to retard the cure
of the resins and act as centers of subsequent deterioration during
heat aging. To check this hypothesis, bonds of aluminum were made with
FPL-878 adhesive by precuring the adhesive for 15 minutes at 275° F. in
atmospheres of oxygen, air, and nitrogen. If the formation of peroxides
or similar intermediates were the cause of subsequent deterioration,
precuring in oxygen would likely cause such compounds to form more
readily and precuring in nitrogen would retard their formation. The
results of these experiments showed there was no real improvement in
the joint strength of bonds at room temperature after aging 16 hours
at 550° F. when precured in nitrogen over those precured in air or in
oxygen.

Precured for 15 minutes at 275° F.	Shear strength[1] at 80° F. after 16 hours at 550° F.
	P.s.i.
In air	312
In oxygen	548
In nitrogen	468

[1] Each value is the average of 5 test specimens.

The actual chemical reactions in curing a combination of two different
resins, each of varying polymer sizes, is understandably complex. It
is quite likely that changes in the precuring as well as curing tempera-
tures could cause variations in the rates of the curing reactions of
these resins with themselves and with each other. Such precuring tem-
perature effects on these reactions could be another possible explana-
tion for the observed dependence of heat resistance of the bonds on the
precuring conditions. The higher precure temperatures presumably could
cause the epoxy resin to react first with the uncured and relatively
small phenol resin molecules and thus retard the further condensation
and cure of the phenol resin with itself to form a highly infusible and
insoluble polymer. However, a study of the effect of adhesive composi-
tion revealed (table 3) that adhesives composed of phenol resins alone
(Formulas A and B) showed definite signs of deterioration at 550° F.
after a precure at 275° F. for 15 minutes as did the adhesive composi-
tions of phenol and epoxy resins (Formulas C to I) under similar con-
ditions as shown by the presence of discolored spots in the adhesive
bond. At a precure temperature of 200° F. for 30 minutes there was no
evidence of the spots characteristic of thermal deterioration in the
aluminum bonds for any of the adhesive formulations. Epoxy resin,
Epon 1007, used alone in formula J as an adhesive and applied as a
solution in ethyl acetate showed no visible spots of thermal deteriora-
tion at either precure condition. The addition of varying amounts of

epoxy resins (Formulas C to G) to the phenol resin in different adhesive formulations showed no particular trend in the effect of the ratio of phenol resin to epoxy resin in the thermal resistance of bonds precured at 275° F. The use of a lower molecular weight epoxy resin (Epon 1001), with approximately the same number of reactive epoxy groups on the resin molecule as the Epon 1007 resin and considered to be more reactive with the phenol resin because of the lower molecular weight, did not materially increase or decrease the amount of thermal deterioration observed in the broken bonds (Formulas H and I) although joint strengths after heat aging were much lower when Epon 1001 was used. The use of methyl ethyl ketone solvent in formula G gave results similar to those obtained with ethyl acetate solvent (Formula E).

The work on adhesive compositions indicated that the resistance of an adhesive composed of phenol and epoxy resins to thermal deterioration was not only dependent upon the precure conditions but also suggested that the phenol resin in the composition might be the source of initial deterioration; spots of deteriorated resin occurred in the bonds when phenol resin was used alone as the bonding agent and no degradation was observed on straight epoxy resin bonds.

Subsequent studies were directed toward learning what possible effect the precure temperature could have on the thermal resistance of a phenol resin, Durez 16227, with various catalyst systems, but without any epoxy resin, when employed as the bonding agent for aluminum. The data in table 4 showed that the resistance to thermal aging of FPL-878 adhesive after precuring for 15 minutes at 275° F. could be improved by addition of certain agents which could be considered as catalysts. In tests at room temperature, after aging 16 hours at 550° F., of the bonds made with formulations of unmodified phenol resin, resin with 0.7 percent benzene sulfonic acid, resin with 0.7 percent benzene sulfonic acid and 5 percent hexamethylenetetramine, and resin with 1.5 percent aminopropyl morpholine, there were brown spots characteristic of thermal deterioration in the adhesive bonds given a precure of 15 minutes at 275° F. This was indicated in the table by increased percentages of discolored areas in the bond. These spots were not noted in any of the bonds precured at 200° F. In all cases where significant spots of deterioration occurred the joint strengths were significantly lower than bonds with little or no such spots except in the formulation with 1.5 percent aminopropyl morpholine, which showed only a slight reduction in strength. Adhesive formulations with 1 percent of phenol, 1.5 percent pyridine, 1.5 percent diethylethanolamine, and 1.5 percent triethanolamine showed no spot deterioration at either precure condition. The joint strength data considered with the appearance of the broken bonds show then that the resistance of this particular phenol resin to thermal degradation was not improved by the addition of either an acid, formaldehyde, or a primary amine (aminopropyl morpholine), but was improved by the addition of phenol and the mildly alkaline tertiary amines (pyridine, diethylethanolamine, and triethanolamine); however, triethanolamine had an adverse effect in reducing joint strength under all test

conditions without contributing to visible thermal deterioration. In tests made immediately at 500° F., the strength of bonds given a precure for 15 minutes at 275° F. were higher than those pre-cured 30 minutes at 200° F. except when benzene sulfonic acid (B.S.A.), B.S.A. and hexa, and diethylethanolamine were used. The addition of an acid catalyst and formaldehyde to the adhesive resulted in no im-provement in the resistance to thermal deterioration and greater loss in immediate strength at 500° F.; the addition of phenol and certain alkaline amine catalysts improved the resistance to thermal degradation as well as the resistance to thermal softening at elevated temperatures. The results of these tests therefore indicate that the adverse effect of the higher precure temperature and long precure periods in reducing the resistance to thermal degradation and the immediate strength at elevated temperatures could very likely be related to the composition and catalytic system of the phenol resin. The following hypothesis was postulated for these observed adverse effects of excessive precure:

The higher precure temperatures and longer precure periods presumably cause excessive liberation of ammonia, which is probably present in the phenol resin either as the original catalyst or from the breakdown of hexamethylenetetramine, added as a latent curing agent, to make the adhesive system less basic or even slightly acid. Under such conditions of reduced alkalinity, the ratio of phenol to formaldehyde is known to be highly important in regulating the final degree of cure and the solu-bility and fusibility of the cured polymer. Carswell[2] reports that when phenol is present in excess, the resin will cure to a completely insolu-ble and infusible form in the presence of an alkaline catalyst, but under similar conditions a soluble and fusible polymer is formed with an acid catalyst. This hypothesis could then explain the lower strength of bonds at elevated temperatures as a result of the more extensive precure periods. The explanation for the occurrence of spots of thermal deteri-oration in the adhesive is more obscure. However, since the thermal deterioration was found to persist under acid catalyst conditions and not under alkaline conditions when a high temperature precure was em-ployed, the cause of thermal deterioration may be associated with an incomplete crosslinking reaction and the formation of some type of thermally unstable compound or group attached to the polymer chain under slightly acid or even nearly neutral curing conditions. The thermally unstable compounds or groups that are formed could then conceivably act as nuclei to trigger the deterioration of the adhesive during heat aging.

Further work is needed to more completely resolve the problem of the effect of precure on the resistance of an adhesive to thermal deteriora-tion. However, the present study has indicated that the real explana-tion may be found in the composition and catalyst system of the phenol resin, which if completely understood could result in the development of metal-bonding adhesives with greatly improved heat resistance. This

suggests the desirability of investigations of various types of phenol resins as heat-resistant adhesives for metal bonding.

DETERIORATION OF STAINLESS STEEL BONDS

The performance of a phenol-epoxy type adhesive, FPL-891, in the preliminary work on this project in bonding aluminum was found to differ in many respects from that in bonds of stainless steel. The data in table 1 showed that the type of surface preparation and the atmosphere of exposure were both highly important variables affecting the thermal resistance of the adhesive bond in stainless steel. These data showed that for stainless steel the sulfuric acid-oxalic acid method (Method B, Appendix) of surface treatment gave better initial bond strengths and better thermal resistance properties than the sulfuric acid-sodium dichromate method (Method A, Appendix). The generally inferior performance of stainless steel bonds as compared to the aluminum bonds in these tests indicated quite definitely that the stainless steel contributed in some way to the degradation of the adhesive bond.

In further work on bonding of stainless steel the effect of various lengths of time of aging, ranging from 1 hour to 200 hours at 550° F. was investigated on lap shear specimens of 0.20-inch T302, 1/2 hard stainless steel bonded with adhesive FPL-878. The results of these tests at room temperature after aging are shown in figure 4 along with similar data on bonds of 0.064-inch 24ST-3 clad aluminum alloy. The aluminum surfaces were prepared for bonding by the standard sulfuric acid-sodium dichromate (Method A, Appendix). The stainless steel was prepared by treating with sulfuric acid-oxalic acid (Method B, Appendix), since previous work had shown these methods to be the most suitable for these two metals. In the bonding process on both metals a precure of 30 minutes at 200° F. was employed to reduce to a minimum the effect of precure on thermal resistance.

Bonds of both metals showed significant losses in strength after the first hour of aging at 550° F. The aluminum bonds, however, showed very little further loss in continued aging up to 200 hours. The strength of the stainless steel bonds, on the other hand, continued to decrease sharply with time until nearly all strength was lost after 48 hours of aging at 550° F. The drop in strength of the steel bonds with time was directly related to increases in the areas of darkened or discolored adhesive. This discoloration was first observed in the broken joints around the edges of the lap joints exposed for short periods and then progressed inwardly on longer exposure until it included the entire bonded area. There was no visible evidence in the aluminum bonds to indicate such progressive thermal degradation of the adhesive. Neither was the degradation of the adhesive in stainless steel bonds similar to the discolored spot-type deterioration observed in aluminum joints that were precured under adverse conditions, as previously described. These

data and observations on the FPL-878 adhesive, like the data on FPL-891 adhesive previously cited, pointed to the stainless steel surface itself or to oxides of some component of the steel surface as possible agents for influencing the deterioration of the phenol-epoxy resin adhesives under heat aging. At least two possible mechanisms for this effect could be postulated:

1. The metal surface itself may be chemically active and may influence the adjacent organic adhesive film catalytically. Presence of adsorbed ions on the metal surface and of alloying elements may be of particular importance in such catalytic effects on the adhesive film. This was one reason chelating agents and other stabilizers were considered in the earlier development of heat-resistant adhesives at this Laboratory.[1]

2. The nature of the metal surface may be particularly important because of physical and chemical changes in the metal layers themselves during the heat aging of the bond. There is little doubt that the metal is covered with a surface oxide coating. In the case of aluminum this oxide layer is believed to form rapidly and rather completely by the time bonding is completed and to possess a rather high cohesive strength. It is then probable that relatively little change in the amount or form of oxide coating occurs on heat aging of the bonds. Based on the relatively slight difference observed in aging aluminum bonds in air and in nitrogen (table 1), it might be inferred that the oxide coating on aluminum retards entry of oxygen from the air quite effectively and thus minimizes further oxidation of the aluminum and of the adhesive film on heat aging. However, in the case of stainless steel, the formation of an oxide coating may be slower and quite incomplete when the bond is formed and may continue to a considerable extent during subsequent heat aging of the bond. This further oxidation may result in a more porous film, perhaps of lower cohesive strength than that formed on aluminum. Such a porous film could be expected to permit greater entry of oxygen into the metal and to the adhesive film, which would result in progressive oxidation of either the metal or the adhesive film on heat aging. The lower cohesive strength of the oxide layer could also contribute to lower overall bond strength after heat aging.

Further work in bonding stainless steel was directed towards exploring these hypotheses, particularly to investigate methods of preparing stainless steel surfaces for bonding that would result in more thermally stable bonds. Adhesive FPL-878 (Appendix) was used throughout in these studies to bond 0.020-inch, 1/2 hard, T302 stainless steel. Bonds were precured for 30 minutes at 200° F. and then pressed at 320° F. for 60 minutes at 50 pounds per square inch bonding pressure. Specimens had an overlap of 0.5 inch.

Effect of Surface Preparation

The results of aging tests at 500°, 530°, and 550° F. on stainless steel bonded with FPL-878 adhesive and prepared for bonding by various methods are presented in tables 5, 6, and 7.

The tests of bonds aged at 500° F. for 48 hours (table 5) and then tested at room temperature showed that a chemical treatment by Method D consisting of hydrochloric acid, hydrogen peroxide, and formalin was superior to Method B (sulfuric acid-oxalic acid) and to Method B followed by Method A (sulfuric acid-sodium dichromate). Heat treating the chemically cleaned surfaces by heating for 1 hour at 500° F. to dry the surface completely and remove any residual acid from the surfaces showed marked improvement only with Method B (Groups 1, 2, and 3). The improvement noted with Method B by heating at 500° F. was probably not a result of the removal of water and adsorbed acids from the surface, but more likely the result of the formation of a stable oxide layer on the metal surface by thermal oxidation since this chemical treatment is a strong reducing agent and could have conceivably removed the naturally occurring oxide from the stainless steel surface. Heating the treated surfaces for 30 minutes at 1200° F., however, showed no more improvement than heating at 500° F. In groups 13, 14, and 15, the stainless steel surfaces, which were first treated with sulfuric-oxalic acid followed by the sulfuric-dichromate solution, were modified by either sprinkling with aluminum powder (13) or brushing with a solution of manganese napthenate (6 percent manganese) (14), or cobalt napthenate (6 percent cobalt) (15). These metallic napthenates were in solutions in organic solvents as supplied by the manufacturer for use as wood preservatives or paint dryers. They were reported to contain 6 percent of the appropriate metal ion by weight. These napthenates were used simply as a convenient means of applying the desired metals to the stainless steel surface. These coated surfaces were then fired at 1200° F. for 30 minutes to remove the organic components and leave the metallic component of the solution possibly combined with the stainless steel on the surface. These tests revealed that aluminum powder (13) had very little advantage over firing alone (3), the manganese had possible adverse effect (14) and cobalt (15) improved the resistance of FPL-878 to thermal degradation to a very marked degree. The effectiveness of the fired cobalt napthenate surface in reducing thermal degradation at 500° F. was considered to be a highly significant step toward improved bonds in stainless steel. These results indicated the desirability of further study of the use of other metallic ions to stabilize the stainless steel surface against thermal aging.

In subsequent work on bonding stainless steel, various metal naphthenates were used to treat the steel surfaces and an evaluation of their effectiveness in reducing thermal degradation of the adhesive was made at 530° F. These data are shown in table 6. Comparison of the results on cobalt-treated surfaces, group 16 (table 6) with group 15 (table 5) showed that an increase of 30° in aging temperature had a marked adverse

effect on the thermal resistance of the stainless steel bond with FPL-878 adhesive. Surfaces coated with iron naphthenate (17) had significantly higher bond strengths after heat aging than did the cobalt-treated surfaces (16). Surfaces treated with lead naphthenate (18) were exceptionally low in strength and most likely indicated that the lead residue, presumably an oxide, was a definite catalyst to thermal degradation of the adhesive. A treatment with zinc naphthenate (19), on the other hand, was superior to the other metallic treatments and indicated a definite stabilizing effect. Methods involving immersion of the acid-cleaned surfaces in boiling 5 percent solutions of cobalt nitrate (20) and cobalt chloride (21) were much inferior to other methods.

Another series of tests (22-27) employed the more promising acid process of hydrochloric acid, hydrogen peroxide, and formalin (Method D, Appendix) as the initial treatment of the steel surfaces. The metal was then coated with various metal naphthenates and fired at 1200° F. before cooling and bonding. These tests again pointed out the superior performance of the zinc-treated surfaces (24) over cobalt (23) and the very adverse effect of treating the surfaces with either lead or copper. These test results again indicated that the effectiveness of the metal treatment on the heat resistance of the bond may be related to the type of chemical treatment employed initially in preparing the steel surfaces.

Results of further study of the resistance of stainless steel bonds to aging at 550° F. are shown in table 7. In this work a more extensive study was made of steel surfaces treated with naphthenates of zinc, cobalt, calcium, iron, and nickel which were fired at 1200° F. for 30 minutes and cooled prior to bonding with FPL-878 adhesive. The superiority of the zinc naphthenate treatment in reducing the thermal degradation of the adhesive compared to other metallic treatments is apparent from these data. The effect of initial chemical treatment of the surface on the subsequent effectiveness of the zinc surface is also apparent from the results of group 34 compared with groups 40, 42, and 44, which indicate that oxidizing chromate solutions, such as those used in Methods A and E, are more favorable than a hydrochloric acid oxidizing solution, such as that used in Method D. Results of tests on groups 44 and 42 show that 1 brush coat of zinc naphthenate was as effective as 2 coats. Zinc napthenate was also effective in two-coat applications where the first coat was of cobalt (46) or nickel (49), but was less effective with calcium (52). One-coat applications of certain mixtures of several naphthenates were promising, particularly a mixture of zinc and nickel napthenates (51) and a mixture of iron, nickel, and zinc napthenates (61). The performance of bonds to stainless steel prepared with mixtures of the metallic naphthenates would probably be worthy of further investigation, especially since little is known of the resistance of a bond of a stainless steel surface treated with zinc to attack by salt water, water, and various aircraft fuels and lubricants.

The examination of the bonds of stainless steel with the zinc-treated surface after aging and testing disclosed that there was still considerable degradation or discoloration of the adhesive occurring around the edges of the lap joints and along the branches of the tunnel-like voids, and in some cases in spots as was observed in bonds to aluminum (fig. 3, B, C, and D) prepared under adverse precure conditions. This observation indicated that the thermal resistance of the adhesive in the stainless steel bond might be improved by dipping the metal in zinc naphthenate, instead of brushing, to more effectively coat the edges of the metal as well as the faces and thus retard any thermal deterioration which might be occurring at the edges. The type of failure with the presence of spots of discolored adhesives also indicated that the optimum precure conditions were probably not being employed. The results of further tests to study such a dipping treatment and various precure conditions on the resistance of FPL-878 adhesive to thermal deterioration are shown below.

Surface[1] treatment	Coating[2]	Precure		Bonding pressure	Shear strength at 80° F. after 48 hrs. at 550° F.[3]
		Temperature	Time		
		°F.	Min.		P.s.i.
D and E	zinc naphthenate	200	30	25	896
D and E	.......do.......	200	30	50	968
D and E	.......do.......	180	25	25	911
D and E	.......do.......	180	30	50	1,080

[1] Methods of surface treatment are described in appendix.

[2] After 1 dip coating the surfaces were heated to 1200° F. for 30 minutes then cooled before the adhesive was applied.

[3] Each value is the average of 8 specimens.

These results showed improved resistance to thermal aging by the dipping process and precure at a slightly lower precure temperature compared to groups 44 and 45 in table 7. Applying the zinc naphthenate by dipping individual metal strips prior to firing and then bonding instead of brushing appeared to reduce the thermal deterioration around the edges of the bonded area and the lower precure temperature of 180° F. eliminated all of the spot-type thermal deterioration in adhesive bonds. The joint strength of 900 to 1,000 pounds per square inch after aging, as was obtained in several of these conditions with zinc naphthenate,

represents a very significant improvement in the resistance of stainless
steel bonds to aging at elevated temperatures over that obtained by
various chemical treatments alone as were employed in earlier studies
on this project.

Time did not permit further study and refinement of the zinc naphthen-
ate treatment of the stainless steel surfaces for bonding. It is quite
likely that a study to determine the effect of such variables as the
thickness of the zinc coat, firing temperature, firing time, initial
chemical treatment, and mixtures of zinc naphthenate with other metal
salts would result in even greater improvement in the resistance of
stainless steel bonds to heat aging. Modification of the steel sur-
face with other metals and by other processes might also be promising
as means of improving thermal stability of the adhesive bonds.

The study on the thermal deterioration of bonds of stainless steel
indicated that the principle cause of deterioration was probably the
adverse catalytic effect of the oxides of stainless steel on the adhe-
sive. The porosity of the oxide surface of the steel to oxygen was
probably also a factor. This adverse effect could not be significantly
reduced by forming a stable oxide layer on the surface by the usual
chemical treatments in water solution or by heat aging of the metal
alone at temperatures as high as 1200° F. prior to bonding. There was
evidence that even after such measures were taken to form an oxide
layer on the surface, further oxidation of the metal took place during
heat aging, which resulted in deterioration of the adhesive. This
further oxidation apparently occurred first at the edges of the bonded
area that were accessible to air to form a porous oxide that permitted
the entry of air and progressive oxidation of the metal into the center
of the bonded area. The adverse effect of the stainless steel surface
on the thermal resistance of the adhesive was reduced to a marked degree
by a zinc coating; this coating was formed on the surface by treating
it with zinc naphthenate and firing at 1200° F. to remove organic com-
ponents and presumably to form zinc oxide. This type of zinc coating
thus apparently stabilized the steel surface against further oxidation,
which would cause subsequent deterioration of the adhesive, by forming
an impervious jacket over the steel and retarding the entry of air into
the steel. This reduction in oxidation of the steel may indirectly
have also reduced an unfavorable catalytic effect of the normal oxidized
steel surface on the thermal degradation of the adhesive itself.

EFFECT OF AGING UNDER STRESS ON BOND STRENGTH

This phase of the study was intended to investigate the effects of the
physical orientation of the molecular chains of the adhesive polymer
in the cured bond on joint strength of lap joints at several conditions.
The orientation of the molecular chain was attempted by aging bonded

lap joint specimens at an elevated temperature in a stressed or loaded
condition. The results of this work also gave an insight into the
thermoplastic properties of phenol-epoxy resin adhesives, their resist-
ance to creep, and the performance of bonds in conditions closely
representative of service conditions.

The study was conducted on 0.5-inch lap joints of 0.064-inch 24ST-3
clad aluminum alloy bonded with FPL-878 adhesive (Appendix). The metal
was prepared for bonding by Method A (Appendix). The adhesive was pre-
cured 15 minutes at 275° F., cured 60 minutes at 300° F. at 50 pounds
per square inch, and postcured 16 hours at 275° F. The large number of
individual specimens, cut from various panels, were randomly inserted
into each of several representative groups for the following tests.

Shear tests were made at each of several temperatures on specimens aged
for 100 hours at 300° and 400°, both unstressed and under a stress of
1,500 pounds per square inch. The results of these tests are shown in
table 8.

The results of these tests showed that aluminum bonds of FPL-878 adhe-
sive, that had been aged at 300° or 400° F. for 100 hours under a stress
of 1,500 pounds per square inch, were approximately 30 percent higher
in strength at -70° F. and at 80° F. than specimens that were aged at
these temperatures in an unstressed condition. At a test temperature
of 300° F. the aged-stressed specimens were about 10 percent higher in
strength than the aged specimens under no stress. At a test temperature
of 600° F. there appeared to be no significant differences in the
stressed and unstressed specimens.

With but one exception the strength values of aged-stressed specimens
were higher than the controls at test temperatures of -70°, 80°, and
300° F. In all cases at these test temperatures the strength values of
specimens aged without stressing were lower than the control strength
values.

The increases of strength values in bonds tested at 600° F. after aging
probably indicated the effect of additional curing of the adhesive dur-
ing the aging period, particularly when aged at 400° F. and showed no
advantage in stressing of the bond during aging.

No creep was observed in any of the bonds by microscopic observation of
scratch lines on the sides of the specimens while under load during the
100-hour aging and loading period at 300° F. and 400° F.

These data showed an apparent advantage in stress-aging bonds at an
elevated temperature. The increase in strength could presumably have
been produced by more favorable orientation of the polymer chains of
the adhesive to relieve internal stresses imposed upon it by the eccen-
tricity of loading in a lap-joint specimen, differences in the thermal
expansion or contraction of the metal and the adhesive, and any internal

molecular forces developed between polymer chains during the random orientation of these chains while heat was being applied in the initial bonding process. The joints may also have increased in strength by virtue of the rearrangement of the metal crystal structure to relieve stresses within the metal.

EFFECT OF HIGH-LOW TEMPERATURE CYCLE

Another possible source of physical deterioration of an adhesive bond in service at elevated temperatures is the internal stressing of the adhesive that comes about due to the differential thermal expansion and contraction of the metal and the adhesive. To study this effect a group of specimens matched with the specimens used in the study on the effect of aging under stress was employed. A group of 0.5-inch lap-joint specimens of 0.020 inch thick, T302, 1/2 hard stainless steel was also included in the study because steel has a coefficient of thermal expansion that is about one half that of aluminum. These specimens were bonded with FPL-878 adhesive by precuring for 30 minutes at 200° F. and were then cured at 320° F. for 60 minutes under 50 pounds per square inch. The stainless steel was prepared for bonding by Method B (Appendix).

The specimens were exposed to a cycle of 45 minutes at 450° F. and 45 minutes at -55° F. and were tested at -70°, 80°, and 450° F. before cyclic exposure and after 25, 50, and 100 cyclic exposures. The periods of exposure in this cycle were shown to be sufficient to allow the temperature of the metal to come to equilibrium and yet not result in any excessive exposure at either temperature in any one cycle. The specimens were changed from the hot to the cold phases of the cycle and vice versa immediately without allowing to cool or warm to room temperature except overnight and over weekends when they were kept at 80° F. The results of these tests are shown in table 9.

The results of tests at -70° F. and 80° F. show a loss in joint strength in both aluminum and stainless steel bonds after 25 cycles. In the case of aluminum bonds there was no further loss in joint strength by longer exposure to 50 and 100 cycles. The bonds of stainless steel, however, showed further losses in strength after 50 cycles and very marked losses in strength after 100 cycles. These losses in strength in steel bonds are believed to be more likely due to thermal degradation of the adhesive as evidenced by higher percentages of discolored area in the bond with longer exposures rather than to continued stressing of the bond by the high-low temperature cycle. The initial drop in joint strength observed after 25 cycles in both types of specimens indicated that the initial cure of the adhesive had been advanced to a higher degree by this exposure, which would result in embrittlement and loss in strength at -70° and 80° F. The increase in joint strength on

cyclic aging observed at 450° F., which may be associated with reduced thermoplasticity or increased cross linking of the adhesive, is a further indication of the advancement in the degree of cure of the adhesive by exposure to the high-low cycle. The marked loss in joint strength at 450° F. in stainless steel bonds after 100 cycles is again attributed to thermal degradation of the adhesive.

The data show little significant evidence of losses in joint strengths that may be attributed directly to thermal shock or adverse stresses imposed on the adhesive bond by differences in thermal expansion of the metal and the adhesive. It is felt that any relationship that may exist between the thermal expansion of the adhesive and adherend is probably very complex for it is known that the thermal coefficient of expansion varies at different temperature ranges and is also very likely to change as other physical properties, such as curing of the resin or changes in the metal itself, are changed with heat aging.

Table 1.--Effects of aging at 550° F. on lap shear specimens of clad aluminum and stainless steel bonded with FPL-891

| Length of exposure at 550° F. | Atmosphere | Metal | Shear strength at 80° F. | | | |
| | | | Method A[1] | | Method B[2] | |
Hours			P.s.i.	Percent[3]	P.s.i.	Percent[3]
0	....	Aluminum	1,312	38-0	878	96-0
96	Air	....do.....	688	85-3	244	90-79
200	.....do.....	....do.....	624	85-15	....	....
96	Nitrogen	....do.....	784	80-6	320	90-31
200	.....do.....	....do.....	796	73-12	....	....
0	....	Stainless steel	434	100-0	2,018	7-0
96	Air	....do.....	0	100-100	44	100-100
200	.....do.....	....do.....	0	100-100	....	....
96	Nitrogen	....do.....	62	100-56	578	21-81
200	.....do.....	....do.....	26	100-92	....	....

[1] Method A (see appendix) refers to the sulfuric acid-sodium dichromate (oxidation type) method of preparing the metal surface for bonding.

[2] Method B (see appendix) refers to the sulfuric acid-oxalic acid (reduction type) method of preparing the metal surface for bonding.

[3] The first value is the average percentage of bond area which has failed in adhesion to metal. Each value is the average of 10 specimens. The second value is the average percentage of estimated area in the bond showing evidence of discoloration or thermal degradation.

Table 2.--Effects of metal surface treatments for clad aluminum alloy on heat aging properties of joints made with FPL-878 adhesive

Method	Composition of treating solution	Conditions of immersion[1]	Heat treatment[2]	Shear strength at 80° F. Initial: P.s.i.	After 48 hours at 550° F.: P.s.i.	Percent[3]
A-1	6 N-NaOH	80° F. for 1-5 minutes		1,522	916	45
A-1	do	do	1 hour at 550° F.	1,548	1,014	32
A-2	1N-HCl	140° F. for 5 minutes		1,562	1,054	18
A-2	do	do	1 hour at 550° F.	1,656	[4]894	24
A-3	H2SO4 (10 percent by weight)	150° F. for 10 minutes		1,524	1,042	35
A-3	do	do	1 hour at 550° F.	1,580	1,016	20
A-4	H2SO4--20 cc, HF--30 cc, H2O--50 cc	80° F. for 5 minutes		1,470	958	20
A-4	do	do	1 hour at 550° F.	1,590	930	15
A-5	H2SO4--10 grams, Na2Cr2O7--1 gram, H2O--30 grams	150° F. for 10 minutes		2,152	1,306	15
A-5	do	do		2,152	[4]894	5
A-5a	do	do	1 hour at 550° F.	2,216	[4]932	5
A-5b	do	do	(Rinsed in 1 percent H2SO4 and air dried)	170	126	98
A-5c	do	do	(1 hour in boiling H2O and air dried)	892	[4]240	89
A-6	Chromic acid[5] anodize	95° F. for 45 minutes		2,370	[4]522	68
A-6a	do	do	1 hour at 400° F.	2,296	[4]2,002	20
A-6b	do	do	(1 hour in boiling H2O and air dried)	1,026	[4]510	64
A-7	H2SO4--10 grams, oxalic acid--10 grams, H2O--80 grams	190° F. for 10 minutes		1,534	[4]986	87

[1] After immersion in the chemical bath, the metal surfaces were rinsed in cold tap water, distilled water, and then air dried.

[2] The metal was heated at the elevated temperatures and cooled again to room temperature before application of the adhesive.

[3] The percentage value is the estimated percentage of bond area showing discoloration. Each value is the average of at least 5 specimens.

[4] Specimens aged at 550° F. for 200 hours and tested at 80° F.

[5] Method BA-1 in Forest Products Laboratory Report 1842.

Table 3.--The effect of adhesive composition and precure on the joint
strength of aluminum bonds after aging at 550° F.

Formula	Adhesive composition				Solvent[1]	Shear strength[2] at 80° F. after 16 hours at 550° F. when:	
	Durez 16227	Bakelite BV9700	Epon 1007	Epon 1001		Precured 30 minutes at 200° F.	Precured 15 minutes at 275° F.
	Parts by weight of solids					P.s.i.	P.s.i.
A	10				E.Ac.	1,406	812 (36)[3]
B	10	2			...do	1,434	986 (53)
C	10	2	0.5		...do	1,346	1,020 (42)
D	10	2	1.0		...do	1,180	922 (35)
E	10	2	2.0		...do	1,132	584 (78)
F	10	2	4.0		...do	996	822 (31)
G	10	2	2.0		MEK	850	512 (63)
H	10	2		0.5	E.Ac.	774	446 (67)
I	10	2		1.0	...do	710	508 (66)
J			10.0		...do	540	476 (0)

[1] Solvent used to dissolve the resin components and to thin adhesive for application by brush. E.Ac. is ethyl acetate. MEK is methyl ethyl ketone.

[2] Each value is the average of 5 specimens.

[3] The value in parentheses is the percentage of bond area showing discoloration or thermal deterioration. The percentage of bond area showing deterioration in bonds precured at 200° F. for 30 minutes was 10 to 20 percent which was the area occupied by the branches of tunnel-like voids with no spot-type deterioration present.

Table 4.--The effect of phenol resin composition and precure on the joint strength of aluminum bonds after aging at 550° F. and immediately at 500° F.

Composition[1]	Precure		Shear strength[2]		
	Minutes	°F.	Initially at 80° F. P.s.i.	At 80° F. after 16 hours at 550° F.[3] P.s.i.	Immediately at 500° F. P.s.i.
1 None	30	200	1,704	1,410 (13)	672
	15	275	1,764	1,020 (38)	590
2 0.7% Benzene Sulfonic acid (BSA)	30	200	1,554	1,446 (14)	920
	15	275	1,516	986 (32)	776
3 0.7% B.S.A. and 5.0% hexa	30	200	1,896	1,154 (22)	554
	15	275	2,040	978 (44)	406
4 1.0% phenol	30	200	1,606	1,308 (18)	650
	15	275	1,694	1,324 (18)	744
5 1.5% pyridine	30	200	1,726	1,606 (19)	846
	15	275	1,840	1,630 (22)	976
6 1.5% diethylethanolamine	30	200	1,876	1,564 (19)	926
	15	275	1,720	1,470 (20)	828
7 1.5% triethanolamine	30	200	1,156	840 (21)	436
	15	275	1,286	994 (20)	486
8 1.5% animopropyl morpholine	30	200	1,566	1,510 (14)	864
	15	275	1,586	1,442 (37)	1,140

[1] Phenol resin, Durez 16227, was used as the bonding agent. The percentages of other materials added were based on the weight of the phenol resin solids. Hexa is hexamethylenetetramine.

[2] Each value is the average of 5 specimens.

[3] The values in parentheses are percentages of bond area showing discoloration or thermal deterioration.

Table 5.--Shear strength values after aging at 500° F. of bonds made
with FPL-878 adhesive on T302 stainless steel treated
with various methods before bonding

Group:	Surface treatment[1]	Heat treatment of surface	Shear strength at 80° F. after 48 hours at 500° F.[2]
			P.s.i.
1	B	None	98
2	B	60 minutes at 500° F.	582
3	B	30 minutes at 1200° F.	550
4	B and A	None	440
5	B and A	60 minutes at 500° F.	540
6	A	30 minutes at 1200° F.	484
7	B and C	60 minutes at 500° F.	100
8	D	None	854
9	D	60 minutes at 500° F.	984
10	B, then 60 minutes in water at 212° F.	None	324
11	B, then 60 minutes in 5 percent CrO_3 at 212° F.	None	0
12	1, then 60 minutes in 2 percent 3-hydroxy-2-naphthoic acid at 212° F.	None	364
13	B, A, then coating of aluminum powder	30 minutes at 1200° F.	550
14	B, A, then 1 coat of manganese naphthenate	30 minutes at 1200° F.	304
15	B, A, then 1 coat of cobalt naphthenate	30 minutes at 1200° F.	1,114

[1] See Appendix for description and composition of the various methods used in surface treatment.

[2] Each value is the average for 3 specimens.

Table 6.--Shear strength values after aging at 530° F.
of bonds made with FPL-878 adhesive on T302
stainless steel treated by various methods

Group	Surface treatment[1]	Coating[2]	Shear strength at 80° F.[3] after 48 hours at 530° F.[2]
			P.s.i.
16	B and A	cobalt naphthenate	192
17	....do....	iron naphthenate	392
18	....do....	lead naphthenate	60
19	....do....	zinc naphthenate	606
20	....do....	cobalt nitrate[4]	60
21	....do....	cobalt chloride[4]	20
22	D	none	380
23	....do....	cobalt naphthenate	362
24	....do....	zinc naphthenate	520
25	....do....	lead naphthenate	90
26	....do....	copper naphthenate	0
27	....do....	nickel naphthenate	246

[1] See appendix for description and composition of the various methods used in surface treatment.

[2] In each case the coating was applied by brush to the chemically treated surfaces and then heated to 1200° F. for 30 minutes and cooled before the adhesive was applied.

[3] Each value is the average for 3 specimens.

[4] The treated metal surfaces were immersed for 60 minutes in a boiling 5 percent solution and then heated to 1200° F.

Table 7.--Shear strength values after aging at 550° F.
of bonds made with FPL-878 adhesive on T302
stainless steel treated by various methods

Group	Surface treatment[1]	Coating[2]	No. of coats	Shear strength at 80° F. after 48 hours at 550° F.[3]
				P.s.i.
28	B	none		152
29	D	none		154
30	....do....	cobalt naphthenate	1	133
31	....do....	iron naphthenate	1	55
32	....do....	calcium naphthenate	1	127
33	....do....	nickel naphthenate	1	85
34	....do....	zinc naphthenate	1	350
35	D and A	none	1	114
36	....do....	cobalt naphthenate	1	40
37	....do....	iron naphthenate	1	236
38	....do....	calcium naphthenate	1	350
39	....do....	nickel naphthenate	1	40
40	....do....	zinc naphthenate	1	660
41	abraded	..........do..........	2	100
42	E	..........do..........	2	504
43	D and E	none		70
44	....do....	zinc naphthenate	1	570
45	....do....	..........do..........	2	580
46	....do....	cobalt naphthenate and zinc naphthenate	1 each	724
47	....do....	zinc naphthenate and cobalt naphthenate	1 each	224
48	....do....	cobalt-zinc naphthenate mixture	1	492
49	....do....	nickel naphthenate and zinc naphthenate	1 each	610
50	D and E	zinc naphthenate and nickel naphthenate	1 each	424
51	....do....	nickel-zinc napthenate mixture	1	600
52	....do....	calcium napthenate and zinc naphthenate	1 each	246
53	....do....	zinc napthenate and calcium naphthenate	1 each	124
54	....do....	calcium-zinc naphthenate mixture	1	140
55	....do....	iron-zinc naphthenate mixture	1	340
56	....do....	cobalt-nickel-zinc naphthenate nickel	1	320
57	....do....	cobalt-calcium-zinc naphthenate mixture	1	500
58	....do....	cobalt-iron-zinc naphthenate mixture	1	556
59	....do....	calcium-iron-zinc naphthenate mixture	1	262
60	....do....	calcium-nickel-zinc naphthenate mixture	1	306
61	....do....	iron-nickel-zinc naphthenate mixture	1	702
62	....do....	iron-nickel-calcium-zinc naphthenate mixture	1	334
63	....do....	iron-nickel-calcium-cobalt-zinc naphthenate mixture	1	320

[1] See appendix for description and composition of surface treatments.

[2] Coatings applied by brush and then heated to 1200° F. for 30 minutes before application of the adhesive. Where more than 1 material was applied the first material mentioned was applied first to the stainless steel surface.

[3] Each value is the average of 4 to 8 specimens.

Table 8.--Effects of heat aging for 100 hours at 300° and at 400° F. in unstressed and stressed conditions on aluminum lap specimens, bonded with FPL-878

Test temperature	Controls[1]	300° F.[2]		400° F.[2]	
		Stressed[3]	Unstressed[4]	Stressed[5]	Unstressed[6]
°F.	P.s.i.	P.s.i.	P.s.i.	P.s.i.	P.s.i.
-70	1,648	2,116	1,554	....	....
80	1,740	2,176	1,592	2,242	1,650
300	2,062	2,290	2,046	1,840	1,610
600	374	440	400	824	900

[1] Specimens not aged or stressed but tested immediately after reaching temperature equilibrium as shown. Each value is the average of 5 specimens.

[2] Each value is the average of 3 specimens.

[3] Specimens aged at 300° F. for 100 hours at a shear stress of 1,500 pounds per square inch.

[4] Specimens aged at 300° F. for 100 hours in an unstressed condition.

[5] Specimens aged at 400° F. for 100 hours at a shear stress of 1,500 pounds per square inch.

[6] Specimens aged at 400° F. for 100 hours in an unstressed condition.

Table 9.--Effect of high-low temperature cyclic exposures on aluminum and stainless steel lap specimens bonded with FPL-878 adhesive

Type of metal	Number of cycles[1]	Average[2] shear strength at:		
		-70° F.	80° F.	450° F.
		P.s.i.	P.s.i.	P.s.i.
Aluminum alloy--24ST3	0	1,704	1,586	1,024
	25	1,410	1,096	1,446
	50	1,534	1,100	1,336
	100	1,530	1,248	1,346
Stainless steel--T302, 1/2 hard	0	2,782	2,748	1,220
	25	1,960	2,074	1,534
	50	1,826	1,874	1,548
	100	1,046	1,316	916

[1] One cycle consisted of 45 minutes exposure to 450° F. then 45 minutes to -55° F.

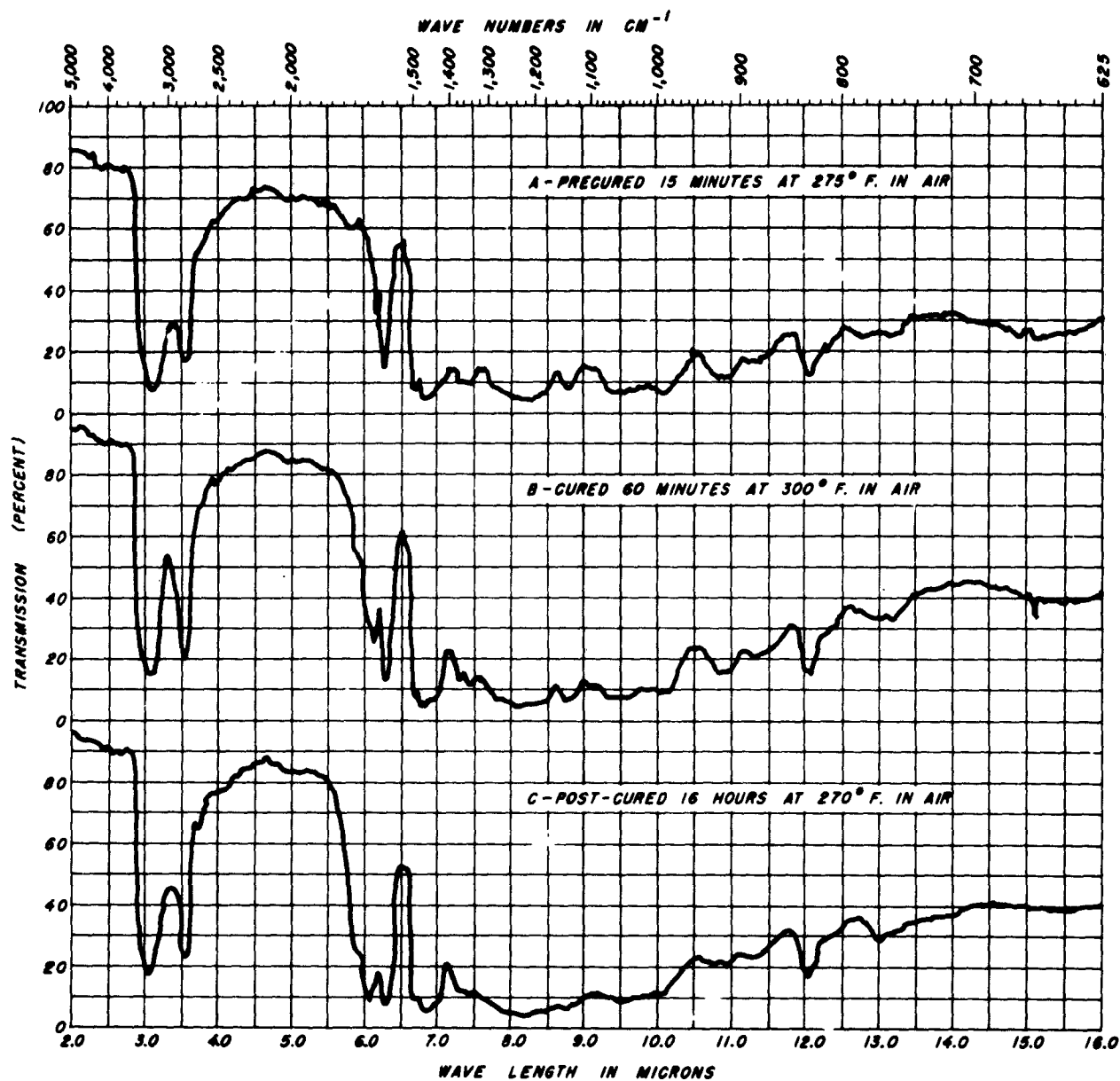[2] Each value is the average of 6 test specimens.

Figure 1.--Infrared absorption spectra of films of FPL-891 adhesive. The curves
have been smoothed out for reproduction purposes, but the exact figures have
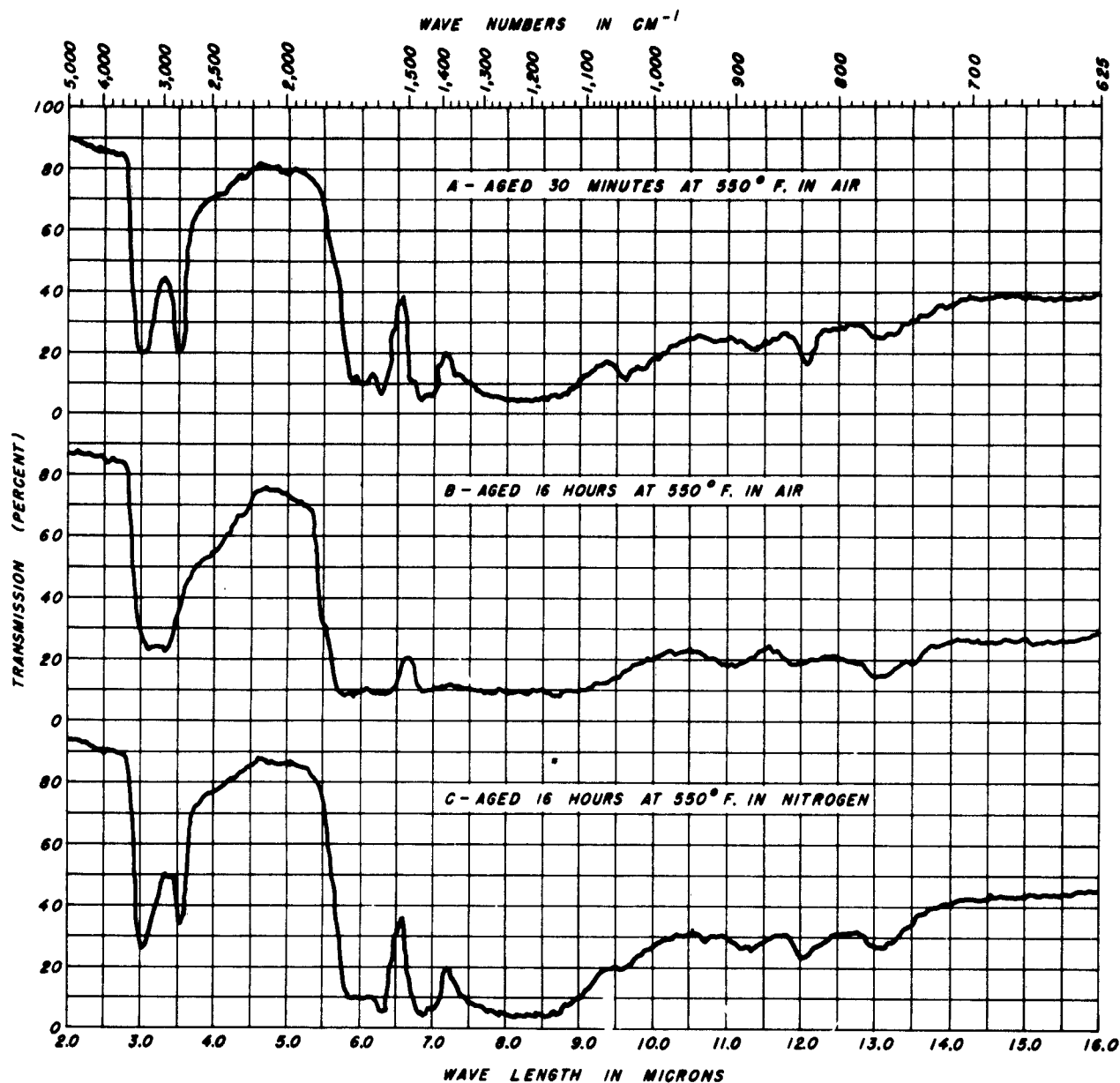been quoted in text.

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Figure 2.--Infrared absorption spectra of films of FPL-891 adhesive. The curves have been smoothed out for reproduction purposes, but the exact figures have been quoted in text.
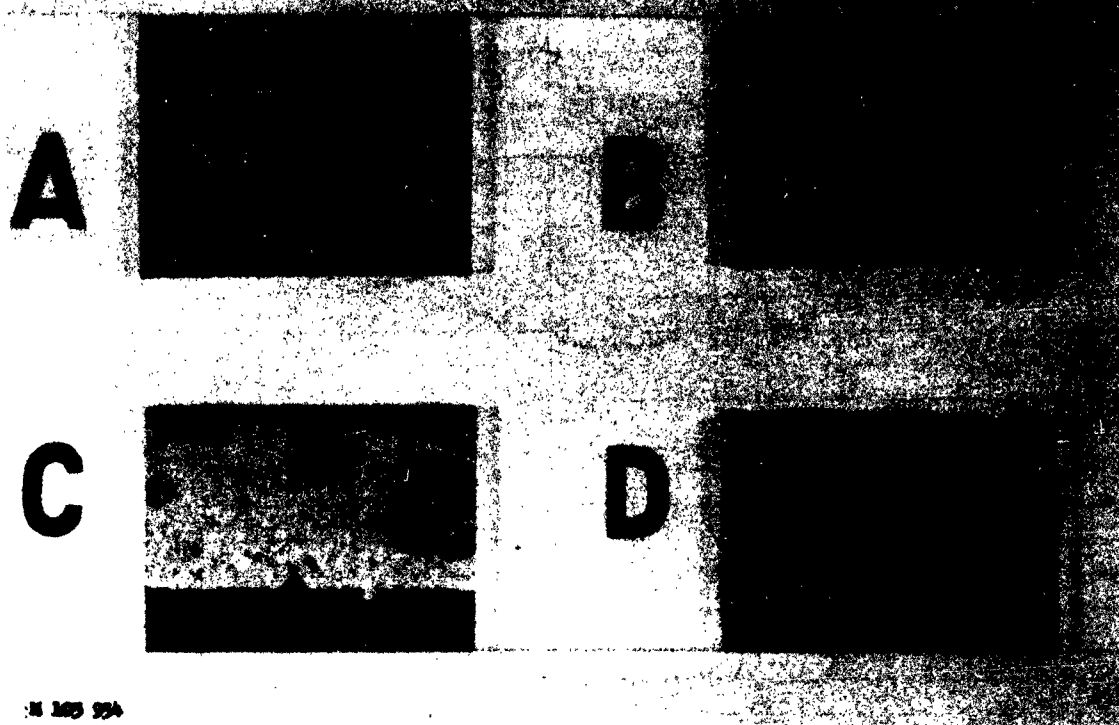
Figure 3. --Bond areas of typical aluminum specimens after aging
at 550° F.: A, no deterioration, high joint strength; B, branched
tunnel-like voids, little deterioration, high joint strength; C, small
spot-type deterioration, intermediate joint strength; D, large spot-
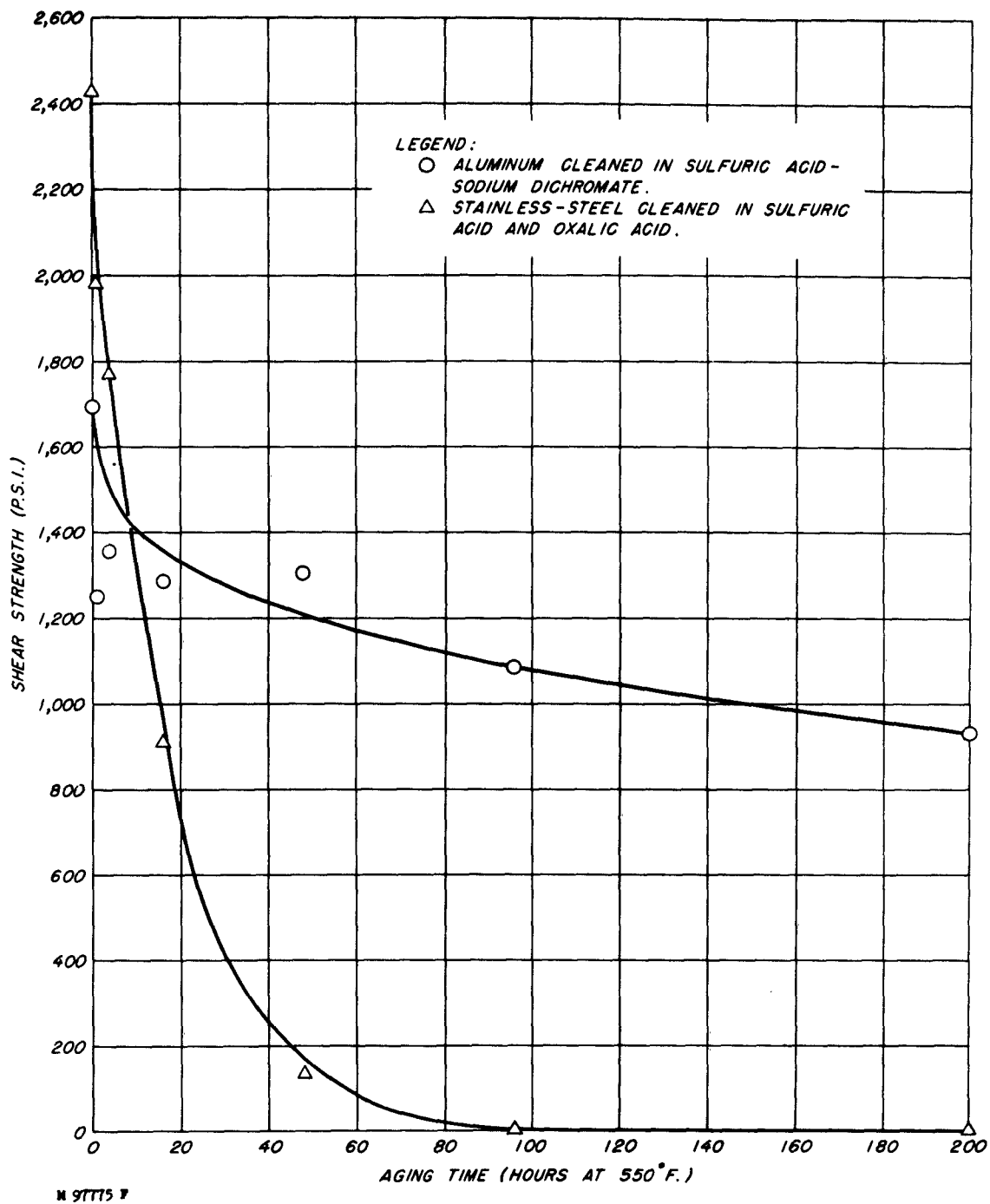type deterioration, low joint strength.

LEGEND:
O ALUMINUM CLEANED IN SULFURIC ACID - SODIUM DICHROMATE.
Δ STAINLESS-STEEL CLEANED IN SULFURIC ACID AND OXALIC ACID.

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Figure 4. --Effect of aging at 550° F. on strength of aluminum and stainless steel bonded with FPL-878 and tested at room temperature.

APPENDIX

Adhesive Formulations

FPL-891 Adhesive

Phenol resin (Durez 16227)	12.5 grams
Epoxy resin (Epon 1001)	2.0 grams
Ethyl acetate	2.0 grams

This formulation was thinned with an equal weight of ethyl acetate before spreading.

FPL-878 Adhesive

Phenol resin (Durez 16227)	12.5 grams
Phenol resin (Bakelite BV9700)	3.3 grams
Epoxy resin (Epon 1007)	2.0 grams
Ethyl acetate	2.0 grams
n-propylgallate	0.2 grams
1-hydroxy, 2-naphthoic acid	0.2 grams

This formulation was thinned with an equal weight of ethyl acetate before spreading.

Methods of Preparing Metal Surfaces for Bonding

Method A

Immersion for 5 minutes at 150° F. in a solution of:

Sulfuric acid (conc.)	100 grams
Sodium dichromate	10 grams
Water	300 grams

Rinse in cold tap water, then in distilled water, and air dry.

Method B

Immersion for 10 minutes at 190° F. in a solution of:

Sulfuric acid (conc.)	100 grams
Oxalic acid	100 grams
Water	800 grams

Rinse in cold tap water, then in steam, and air dry.

Method C

Immersion for 5 minutes at 140° F. in a solution of:

Sulfuric acid (conc.)	100 milliliters
Hydrofluoric acid (50 percent)	150 milliliters
Water	250 milliliters

Rinse in cold tap water, then in distilled water, and air dry.

Method D

Immersion for 10 minutes at 150° F. in a solution of:

Hydrochloric acid (conc.)	100 grams
Hydrogen peroxide (30 percent)	4 grams
Formalin (40 percent)	20 grams
Water	90 grams

Rinse in cold tap water, then in distilled water, and air dry.

Method E

Immersion for 15 minutes at 170° F. to 180° F. in a solution of:

Sulfuric acid (conc.)	100 grams
Sodium dichromate	10 grams
Water	55 grams

Rinse in cold tap water, then distilled water, and air dry.